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(54) A Method of Recovering Lead
Values from Scrap Batteries

(57) Lead is recovered from the paste fraction of scrap lead batteries as a solution of lead nitrate by a wet process which involves a preliminary desulphation of the paste fraction by

treatment with a carbonate or hydroxide of an alkali metal or of ammonium. The solid phase of the reaction product is then treated with nitric acid, to convert into lead nitrate the lead present as metal, as lead monoxide and as lead dioxide, in the presence of hydrogen peroxide or of added lead.

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SPECIFICATION

A Method of Recovering Lead Values from Scrap Batteries

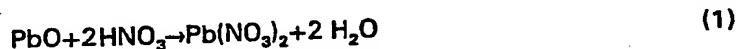
Scrap lead batteries are treated in a battery breaker, which separates the crushed material into three main fractions, one containing the paste, a second containing metal derived from the battery grids and a third consisting of the plastics material constituting the casings and separators. The third fraction is generally waste, the second fraction is subjected to smelting and refining to recover lead and antimony and the first or paste fraction is normally also subjected to smelting and refining.

The paste fraction consists predominatingly of lead sulphate, the next main constituent is PbO_2 and PbO and some metallic lead are also present

We have found that the total lead contents of a series of samples taken from different battery breaking machines varied between 70% and 80% of the solids present in the paste. The amount of lead present as sulphate varied between 24% and 41%, the amount as metal between 1% and 25%, and the amount as lead dioxide between 11% and 26%. All these figures are given as percentages by weight on the solids in the paste. The variations in the amounts of lead as lead sulphate and as lead dioxide arise from variations in the state of charge of individual batteries as they are scrapped. The metallic lead in the paste fraction has its origin partly in the "sponge lead" which constitutes the active material of negative plates in the charged condition, and partly in the ingress of fragments of broken grid alloy into the paste fraction when the battery is broken and its components separated. Sponge lead, when wet, is readily oxidized in the atmosphere, and as a result the paste fraction contains between 2% and 15% of lead monoxide.

The object of the present invention is to avoid the necessity for smelting and to provide a wet process for converting the lead present in the paste fraction at high yield into an aqueous solution of lead nitrate, which is a useful intermediate in the manufacture of lead chromate pigments.

It is not feasible to treat the paste fraction directly with nitric acid because, while metallic lead and lead monoxide both dissolve readily in nitric acid, lead sulphate and lead dioxide do not and must therefore be converted into acid-soluble forms. Lead monoxide dissolves according to the equation:



Metallic lead dissolves in nitric acid producing lead nitrate and a variety of gaseous products including nitrous oxide (N_2O), nitrogen (N_2) and nitric oxide (NO). The proportions of these gases vary according to the temperature and the concentration of the nitric acid, and therefore vary during the course of a dissolution. The dissolution of metal is a slower process than that of lead monoxide at low temperature and at low concentrations of acid.

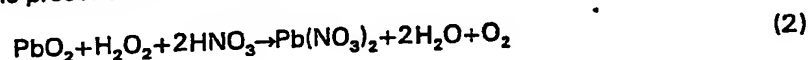
It is therefore necessary to subject the paste fraction to a preliminary desulphation treatment to convert the lead sulphate into a water soluble sulphate and a compound of lead which is soluble in nitric acid. This may be achieved in accordance with the invention by treating the paste fraction either with a carbonate of an alkali metal, e.g. sodium carbonate or potassium carbonate, or with ammonium carbonate to convert the lead sulphate into lead carbonate, which is soluble in nitric acid, or with an alkali metal hydroxide, e.g. sodium or potassium hydroxide, or with ammonium hydroxide, which converts the lead sulphate into a hydrated lead oxide which is also soluble in nitric acid.

This desulphation treatment may be carried out at room temperature, but it may be advantageous in order to speed up the reaction to use a hot solution. Thus the reaction may be carried out at a temperature in the range of 10—100°C.

These are known reactions. Thus U.S. Patent No. 3689253 describes desulphation of battery sludge with an alkali metal hydroxide or carbonate as a preliminary to smelting.

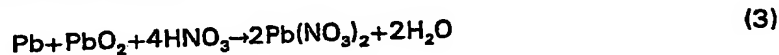
There remains the problem of converting the desulphated battery paste, after removal of the liquid phase, e.g. by filtration, to lead nitrate solution. The desulphated material is soluble in nitric acid apart from the lead dioxide and such minor amount of unconverted lead sulphate as may be present following the desulphation step.

One way of rendering the lead dioxide amenable to treatment with nitric acid in a wet process is to reduce it to lead monoxide. Most reducing agents produce by-products which will contaminate the resulting solution of lead nitrate but we have found hydrogen peroxide to be effective. It reacts as follows with lead dioxide in the presence of nitric acid:—



the oxygen escaping and leaving no contaminant in the lead nitrate.

We have also found that lead dioxide is capable of reacting as follows with nitric acid if lead dioxide and metallic lead are present in the material to be treated in the correct relative proportions, without the necessity of using a reducing agent:—



As a practical matter, the paste fraction is highly unlikely to contain sufficient lead for this reaction to take place and it will normally be necessary to add up to $1\frac{1}{2}$ parts of lead, e.g. in the form of granulated lead or of broken battery grid, by weight per cent weight of lead dioxide. The amount of nitric acid should of course be sufficient for reaction with the lead dioxide, the lead monoxide and all the lead present.

The reaction with nitric acid, in the presence of added lead, requires to be carried out at an elevated temperature in the range of 40—90°C.

The invention accordingly provides a method of recovering lead as an aqueous solution of lead nitrate from the paste fraction derived from scrap lead batteries, which comprises subjecting the paste fraction to desulphation by treatment with a carbonate or hydroxide of an alkali metal or of ammonium, separating the solid and liquid phases of the reaction product, and then treating the solid phase with nitric acid in the presence of hydrogen peroxide, or in the presence of added lead and at a temperature in the range of 40—90°C, to convert to lead nitrate substantially all of the lead present in the solid phase.

While the relative proportions of the different lead values in the paste fraction will inevitably vary from time to time, analysis of the paste fraction from time to time will enable the amount of added lead to be so organised that procedure in accordance with equation (3) will result in recovery of the great bulk of the lead values. All that will be lost is any excess of either lead or PbO_2 , generally the latter, over that which reacts in accordance with equation (3).

The product is an impure aqueous solution of lead nitrate having a pH value of 1—2. Two of the impurities are bismuth and iron, the bismuth being derived from the lead in the batteries and the iron from corrosion of parts of the battery breaking plant. These impurities can be removed by raising the pH of the solution to a value in the range of 3 to 4 by addition of PbO and filtering to remove the compounds of bismuth and iron. The added PbO reacts with excess nitric acid to form lead nitrate and adjustment of the pH value removes dissolved antimony a small amount of which is often present in a lead nitrate solution prepared wholly or in part from grid metal. When reaction of the lead dioxide with nitric acid is effected in the presence of added lead, it may be desirable to oxidize the iron to the ferric state by addition of hydrogen peroxide before adjusting the pH value. Another impurity is copper derived from cable ends, which can be removed by taking advantage of a form of cementation reaction in which a relatively more noble metal is precipitated by a more base metal, in this case metallic lead. Copper nitrate in solution reacts with lead according to the equation:



Copper can therefore be precipitated as metal by addition of lead, as rolled strip, granules or powder. Preferably the removal of copper is effected after iron and other elements have been removed by adjustment of the pH of the solution to 3—4; in this pH range the concentration of free acid is too low for any risk of redissolution of copper to exist.

If sodium carbonate is used for desulphation, the lead sulphate is converted into a double salt, lead sodium carbonate, in which some sodium is chemically combined. The final lead nitrate solution accordingly contains some sodium. For many purposes this sodium can be tolerated; if it has to be removed it is necessary to introduce an extra step in which the desulphated solids are slurried in water and carbon dioxide is passed through before treatment with nitric acid. In Example 8 below, in which the removal of sodium was so carried out, the final solution contained 0.21% of sodium. In example 9, in which sodium was not removed, there was ten times as much.

The purified lead nitrate solution can be concentrated to a desired strength for sale or, alternatively, the lead nitrate can be recovered as crystals from the solution.

In the following Examples, all parts are by weight unless otherwise stated:—

Example 1

10 g of lead dioxide were stirred with 15 g of granulated lead in 100 cm³ of a 20% (w/v) solution of nitric acid for 30 minutes at 60°. The lead dioxide all dissolved in 30 minutes.

Example 2

A similar reaction mixture to that of Example 1 was stirred at room temperature. A clear solution was produced after 2 hours.

These two examples illustrate only the reaction of lead dioxide with nitric acid in the presence of lead. Together they show that the reaction is more rapid at elevated temperatures, and in practice it has been found that in the treatment of actual desulphated battery paste using broken grid metal to dissolve the lead dioxide the rate of reaction at room temperature is unacceptably low.

Example 3

This example concerns a battery paste fraction containing:—

5	Total lead	78.5%	5
	Lead as lead sulphate	28.4%	
	Lead as metal	18.1%	
	Lead as lead dioxide	20.4%	
	Lead as lead monoxide	11.6%	

100 g of the material was stirred for one hour with a solution of 18 g of sodium carbonate in 150 cm³ of water, at room temperature. After filtration the solids were slurried in 300 cm³ of water. Nitric acid was added, in the form of the 70% w/w solution (specific gravity 1.42) until the pH was 1.5. The amount required was 22.5 cm³, which corresponds to 22.5 g of anhydrous HNO₃. It will be noted that this is the approximate equivalent (24.3 g is the calculated equivalent) of those lead compounds, the lead monoxide and the lead carbonate formed from the lead sulphate by the action of the sodium carbonate, that are readily soluble in dilute nitric acid. Next 8.6 g of granulated lead was added to bring the ratio of lead to lead dioxide to 3 parts to 2 by weight, the suspension was warmed to 70°, and a further 37.5 g of nitric acid in the form of 37.5 cm³ of the 70% w/w solution were added. After stirring for two hours, no lead dioxide remained. After filtration there were obtained a residue weighing 10 g (dry bases) and a solution containing 81.8 g of lead as nitrate. Allowing for the 8.6 g of added lead, the amount extracted from the battery material was 73.2 g, representing a yield of 93.2%.

20 Example 4

This example concerns a battery paste fraction containing:—

25	Total lead	72.3%	25
	Lead as lead sulphate	41.6%	
	Lead as metal	3.2%	
	Lead as lead dioxide	25.7%	
	Lead as lead monoxide	1.8%	

100 g of material were treated as in Example 3, with the following changes in the amounts of reagents, made to take account of the different composition. The material was desulphated at 25°C by stirring for one hour with a solution of 26.5 g of sodium carbonate in 150 cm³ of water. The resulting solids were slurried in water, and the pH brought to 1.5 by adding 32 g of nitric acid in the form of 32 cm³ of the 70% w/w solution (26.4 g constitute the equivalent of the lead sulphate and the lead monoxide contents). The temperature was raised to 70° and stirred for two hours with a further 43 g of nitric acid, added in the form of 43 cm³ of the 70% w/w solution, and 30.8 g of granulated lead. There were produced a residue weighing 6 g and a solution containing 102.7 g of lead as lead nitrate. After allowing for the added lead, the amount of lead extracted from the battery paste fraction was 71.9 g representing an extraction of 99.4%.

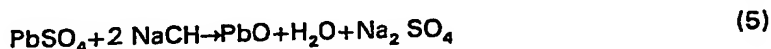
Example 5

This example concerns a battery paste fraction containing:—

40	Total lead	72.7%	40
	Lead as lead sulphate	39.5%	
	Lead as metal	10.7%	
	Lead as lead dioxide	11.4%	
	Lead as lead monoxide	11.1%	

200 g of this material were stirred for two hours with a solution of 33.6 g of sodium hydroxide in 400 cm³ of water, at room temperature. After filtration the solids were slurried at 600 cm³ of water at 60°, and 100 g of nitric acid as HNO₃ were added, in the form of 100 cm³ of the 70% w/w solution (specific gravity 1.42), followed by 30 cm³ of "100-volume" (30% w/v) hydrogen peroxide. After stirring for 30 minutes, the reaction mixture was filtered and a solution of lead nitrate was produced containing 139.5 g of lead, corresponding to a percentage extraction of 95.9%.

The amount of sodium hydroxide used in this example is 110% of the stoichiometric amount required to effect the conversion of lead sulphate to hydrated lead monoxide according to the equation:

**Example 6**

This example concerns the same battery paste fraction as that used in Example 5 and the experimental conditions were the same except that the amount of sodium hydroxide was reduced to

30.5 g. The final percentage extraction of lead as dissolved lead nitrate was 89.9%.

In this example the amount of sodium hydroxide used was exactly the stoichiometric equivalent of the lead sulphate.

Example 7

5 This example concerns the same battery paste fraction as that used in Example 5; it illustrates the use of broken grid metal to take up lead dioxide. 5

200 g of the battery paste fraction was desulphated as described in Example 5 and the solids, after filtration, were slurried in 600 cm³ of water at 70°. A total of 25.3 g of broken grid metal fraction containing 90% of lead, was added, together with 125 g of nitric acid in the form of 125 cm³ of the 10 70% w/w solution. The completion of the dissolution of the lead dioxide was indicated by the disappearance of the characteristic dark brown colour of this substance after 1½ hours. After a further 30 minutes, the reaction mixture was filtered and a solution of lead nitrate was produced containing 156.7 g of lead. After allowing for 22.8 g introduced by the grid metal fraction the amount of lead 15 extracted from the paste fraction in the form of lead nitrate was 133.9 g, representing a percentage yield of 92.1%. 15

Example 8

This example describes the whole process, including the purification of the solution, and gives the amounts of typical impurity elements in the product.

1850 g of battery paste were stirred at room temperature for two hours with 2 litres of water in 20 which were dissolved 390 g of sodium carbonate. The analysis of the battery paste was:— 20

	Total lead	65.7%	
	Lead as lead sulphate	37.5%	
	Lead as metal	2.9%	
25	Lead as lead dioxide	20.2%	
	Lead as lead monoxide	5.1%	25

The desulphated solids were filtered off and reslurried in 2 litres of water. Carbon dioxide was passed through the solution for 4½ hours at a rate of 100 cm³ per minute, to free the solids of combined sodium. The solids were filtered off once more.

Two such portions, representing 3700 g of the original paste, were slurried in 5.5 litres of water 30 and reacted first with 800 cm³ of 70% w/w nitric acid corresponding to 800 g of anhydrous nitric acid. Then 850 kg of broken battery grid alloy containing 94% of lead were introduced, together with a further 1000 cm³ of 70% w/w nitric acid corresponding to 1 kg of anhydrous nitric acid, the 35 temperature was raised to 65°C, and the mixture stirred for four hours. A further 2 litres of water were added before filtration. To the filtrate were added 15 cm³ of hydrogen peroxide, to oxidize iron to the tervalent state. The solution was brought to pH 3.5 by the addition of 47 g of lead oxide (litharge), and 35 filtered.

There were finally obtained 7.400 litres of a solution containing 326 g of lead per litre as nitrate. This was stirred overnight with a small quantity of rolled metallic lead strip to precipitate copper. The solution was then diluted with 0.913 l of water to provide 8.313 litres of a solution of lead nitrate 40 containing 290 g of lead per litre, equivalent to 463 g of lead nitrate per litre. 40

Exhaustive washing of the residue produced a further 221 g of lead nitrate in the form of a dilute solution. The filtration residue weighed 1088 g and contained 45.7% of lead.

A mass balance for lead was drawn up as follows:

<i>Input:</i>			
45	3700 g of battery paste at 65.7%	2431 g	45
	850 g of grid metal at 94.0%	799 g	
	47 g of litharge at	44 g	
		<hr/>	
		3273 g	
<i>Output:</i>			
50	8.313 litres of solution at 290 g l ⁻¹	2411 g	50
	2.980 litres of solution at 74.2 g l ⁻¹	221 g	
	1088 g of residue at 45.1%	497 g	
	unaccounted for	144 g	
		<hr/>	
		3273 g	

55 The analysis of the solution for impurities was as follows, the figures represent the percentage of 55 impurity element calculated on the contained lead nitrate.

Sodium 0.21
Antimony 0.0008

Copper 0.003
Iron indetectable

Example 9

- 500 kg of wet battery paste containing 306 kg of dry solids were sieved with water through a 1/8" stainless steel mesh screen and the volume made up to 3000 litres. 28 kg of plastics waste were retained on the screen. 5

The slurried solids were stirred with 150 kg of sodium carbonate. The suspension was centrifuged and yielded 412 kg of solids and 3000 litres of a solution containing 86 kg of sodium sulphate.

- 10 The original battery paste contained 215 kg of lead, representing a lead content of 70.3% on the dry solids. Included in this were 26.5% of lead as lead dioxide. The iron content was 0.15%. 10

The centrifuged desulphated solids were stirred into 2000 litres of water and 240 kg of 60% nitric acid were added. There were next added 25 kg of 27% hydrogen peroxide, 83 kg of 60% nitric acid, and a further 28 kg of 27% hydrogen peroxide. After 1½ hours stirring the pH of the solution was raised by 3.0 by the addition of 75 kg of litharge. The reaction mixture was then centrifuged. 15

- 15 This yielded 83 kg of wet centrifuge cake containing 54 kg of dry solids; the lead content was 40.7% based on the dry solids. The liquor contained 419 kg of lead nitrate containing 262 kg of lead in 2990 litres; the sodium and iron contents each expressed as a percentage of the contained lead nitrate were 2.1% and less than 0.002%. 15

- 20 The mass balance for lead was as follows:— 20

Input:

306 kg of dry battery paste solids at 70.3%	215.0 kg
75 kg of litharge	69.6 kg
	<hr/>
	284.6 kg

25 *Output:*

2990 litres of solution at 87.8 g l ⁻¹	262.4 kg
54 kg of dry residue at 40.7%	22.0 kg
unaccounted for	0.2 kg
	<hr/>
	284.6 kg

- 30 The yield of lead nitrate from the battery paste was 89.7% 30

Example 10

The battery paste fraction used had the composition stated in Examples 5, 6 and 7, namely:

	Total lead	72.7%	
	Lead as lead sulphate	39.5%	
35	Lead as metal	10.7%	35
	Lead as lead dioxide	11.4%	
	Lead as lead monoxide	11.1%	

- 40 200 g of the material was stirred for two hours at room temperature with a solution containing 37.5 g of commercial ammonium carbonate and 13 cm³ of ammonia solution (35% w/w NH₃) in a total volume of 400 cm³. The solids were filtered off and reacted with nitric acid and hydrogen peroxide as described in Example 5. The final solution contained 137.8 g of lead, corresponding to a percentage extraction of 94.8%. 40

Example 11

- 45 The composition of the battery paste fraction and the conditions of the experiment were as above except that the desulphating solution consisted of 46 cm³ of ammonia solution (35% w/w NH₃) diluted with water to 400 cm³. The yield of lead as nitrate was 112.2 g, corresponding to a percentage extraction of 77.2%. 45

Claims

- 50 1. A method of recovering lead as an aqueous solution of lead nitrate from the paste fraction derived from scrap lead batteries, which comprises subjecting the paste fraction to desulphation by treatment with a carbonate or hydroxide of an alkali metal or of ammonium, separating the solid and liquid phases of the reaction product, and then treating the solid phase with nitric acid in the presence of hydrogen peroxide, or in the presence of added lead and at a temperature in the range of 40—90°C, to convert to lead nitrate substantially all of the lead present in the solid phase. 50

2. A method according to claim 1, wherein the added lead is granulated lead.
3. A method according to claim 1, wherein the added lead is lead derived from broken battery grid.
4. A method according to any one of the preceding claims, wherein the desulphation treatment is
5 carried out at a temperature in the range of 10—100°C. 5
5. A method according to any one of the preceding claims, in which sodium carbonate is used for desulphation and the solid phase is slurried in water and treated with carbon dioxide prior to reaction with nitric acid.
6. A method according to any one of the preceding claims, in which the solution of lead nitrate is
10 purified of bismuth and iron by raising its pH to a value in the range of 3 to 4 by addition of lead
monoxide followed by filtration. 10
7. A method according to any one of the preceding claims, in which the solution of lead nitrate is purified of copper by addition of lead.
8. A method according to claim 1, substantially as described herein with reference to any one of
15 the foregoing Examples 3 to 11. 15

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